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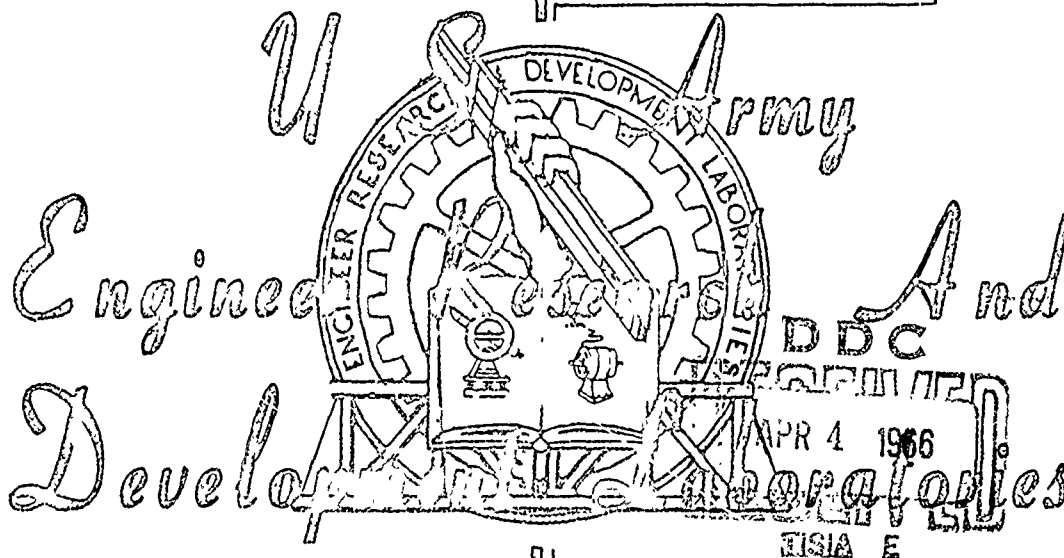## U.S. ARMY MOBILITY EQUIPMENT CENTER

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Authors: Lothar Wöhler and F.Martin

NEW FULMINATES AND
AZIDES

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NEW FULMINATES AND
AZIDES

Lothar Wöhler and F. Martin

The Chemistry Institutes of the Karlsrhue
and Darmstadt Schools
of Techrology.

NEW FULMINATES AND AZIDES

"Chemische Berichte" 1917 Art. 88.

I. Fulminates

The keystone in the investigations on the composition
of fulminic acid was formed by the determination of molecular
weight in the anhydrous sodium salt of fulminic acid. Through
measurement of freezing-point lowering and conductivity of its
aqueous solution, this led to the formula CMONa (ref.1). The
preparation of sodium fulminate was successful through the sim-
ple process of permitting sodium amalgam to act on fulminating
mercury under alcohol.

In addition to mercury and silver fulminate and the an-
hydrous sodium salt --which had already been obtained by Ehren-
berg in hydrous and consequently easily decomposing state --,
simple salts of fulminic acid have so far not become known
although scarcely any other compound has occupied as much as
fulminic acid every decade of the last chemical century (ref.2).
With double conversion in aqueous solution, there are produced,
due to the weak character of fulminic acid, frequently complexes
such as the potassium silver fulminate of Liebig or basic salts
by hydrolytic dissociation. The complicated fulminating-mercury
process (ref.3) for preparation from alcohol and nitric acid
can only be applied to the silver salt but fails already with
the copper salt because here only insoluble salts are stable,
but, due to the oxidation process, only the higher oxidation
stages originate which are generally soluble and are therefore
subject to further decomposition.

Even so, fulminic acid offers an opportunity, like hydra-
zoic acid, by its established simplicity and through knowledge
of the entire series of its salts to investigate the influence
of the degree of affinity of the metallic bases --derived from
the electrochemical series -- on explosive properties, on sen-
sitivity to impact and temperature increase, on generation of
heat, on detonation speed, and on initiating power. However,
the interrelations of these physical constants are in turn of the
greatest importance for the chemistry of explosives just like,
on the other hand, a comparison of these constants in the series
of salts of the fulminates with those of the series of the salts
of the azides is highly pertinent.

We are now successful in applying the method utilized
for the preparation of sodium fulminate by chemical conversion

of fulminating mercury or fulminating silver, through less
noble metals in the form of amalgams, to the preparation of a
large number of new simple and anhydrous fulminates. Due to
the risk of hydrolytic dissociation, this must not be done,
any more than for anhydrous sodium fulminate, in an aqueous
solution -- with the exception of the entirely insoluble cop-
per fulminate -- because free fulminic acid tends greatly to
polymerization and the formation of polymeric salts. Conver-
sion further furnishes the more noble metal from the fulmina-
ting mercury or silver frequently in an inconveniently fine dis-
tribution which considerably interferes with the separation of /588
the new fulminate. When employing sodium amalgam and fulmina-
ting mercury under alcohol, this difficulty could be overcome
but necessitated in other salts a new solvent for the fulminate
created for which dry methyl alcohol has proved itself since
the fulminate can then be precipitated with ether. We were
thus successful in obtaining the fulminates of potassium and
the alkaline earths together with that of manganese (on which
we shall report later) and also those of copper, thallium and
cadmium which, in the chemistry of explosives, are related by
their properties to fulminating mercury and silver as well as
to the azides of the heavy metals and which will therefore be
described here in connection with research on the chemistry of
explosives on which we are reporting simultaneously elsewhere
(ref.4).

Experimental Procedure

The conversion with amalgams takes place in a rubber-
stoppered flask under mechanical shaking with not more than
1-2 g mercury and/or silver fulminate and in dry drydrogen as
does filtration and washing with ether. Drying was carried out
under vacuum over calcium chloride in addition to phosphorus
pentoxide. It is understood that the greatest care must be
exercized in experiments with these highly explosive substances.
In order to avoid local injury from explosion, it is necessary
to work with long-handled tools and with protective glasses and
face mask. These substances should never be stored in glass-
stoppered flasks because the dust particles of some of them de-
tonate already when inserting the stopper and thus ignite the
entire mass in the vessel.

Fulminating mercury was prepared by pouring a solution
of 50 g of metal in 600 g of nitric acid (1.4) with the addition
(for "bleaching" as reported earlier) of 0.6 g each of copper
and hydrochloric acid (1.18) in 600 ccm alcohol (95 %). This
was purified by dissolution in potassium cyanide and reprecipi-
tation under ice cold with nitric acid. Silver fulminate was

obtained and utilized directly from 5 g of metal dissolved in
155 g nitric acid (1.3) through pouring into 150 ccm alcohol
(95%).

The relatively low heat of decomposition under vacuum
of the fulminates and azides was measured in a small calorime-
ter whose walls were lined with glass wool as protection against
the metal projectiles from detonation.

1. Cadmium Fulminate

The required amalgam was obtained in 6 hours from con-
centrated cadmium-sulphate solution over about 50 g of mercury
as cathode in a breaker with 0.8 A, i.e. was about 20-%, and
was repeatedly washed with water and subsequently with methyl
alcohol and finally with some of the latter distilled over
barium oxide, (with a high cover of glass pearls and wool be-
cause the distillate is otherwise difficult to obtain free
from baryte).

2 g of fulminating mercury with the addition of 30 ccm
of anhydrous methyl alcohol under ice cold were shaken with the
amalgam for 25 min until a test of the solution passed through
hardened filter with stannous chloride no longer showed a reac-
tion to mercury. The alcoholic solution of the fulminate be-
comes, without cooling, rapidly yellow through polymerization
and the dry residue even more so after evaporation of the al-
cohol. Filtering was done in a hydrogen stream into anhydrous
ether and further washing was made with the latter. The comple-
tely white fulminate was dried under vacuum. It subsequently
still contains 2% methyl alcohol which is not easily and still
incompletely released only after careful heating for 24 hours
under vacuum to 55° over phosphorus pentoxide.

The demonstration of the alcohol is made after distil-
lation of the fulminate solution in water through the addition
of aqueous silver-nitrate solution for the purpose of precipi-
tating the fulminate and repeated oxidation of the first distil-
late with an electrically heated copper spiral to formaldehyde
which is recognized by the reddish coloration of phlorogluci-
nol in customary manner.

Electrolytic determination of cadmium cannot be made
directly from a potassium-cyanide solution although this me-
thod of determining cadmium was found by us to be excellent
otherwise because the remaining fulminic acid causes values
which are too high due to carbon-containing deposits. Instead,
the metal was determined, after repeated evaporation with sul-
phyric acid and calcining, as sulphate which is also an excel-

lent method of determination. Determination of fulminate was
carried out, similar to the Volhard cyanide analysis, with silver
nitrate in excess which is determined after filtration with
ammonium thiocyanate and ferric potassium sulphate as indica-
tor. However, since silver fulminate dissolves appreciably
in water and thus gives fulminate values which are too low, we
utilized alcoholic silver nitrate and a fulminate solution in
methyl alcohol.

$$Cd(CNO)_2. \quad \begin{array}{l} Ber. \ Cd \ 57.23, CNO \ 42.77. \\ Cef. \quad " \ 56.6, \quad " \quad 42.34. \end{array}$$

Subsequently, the fulminate still contained 1% methyl
alcohol, probably as crystal alcohol, since the residue of the
methyl-alcohol solution was recognized as birefringent under
the microscope during evaporation under vacuum.

When kept dry, the white salt is entirely stable, re- /590
latively soluble in alcohol, easily soluble in methyl alcohol,
and very easily soluble in water but here decomposes easily by
hydrolysis and the absorption of carbon dioxide as well as
through polymerization of the fulminic acid produced.

The heat of decomposition measured in the calorimeter
vacuum amounted to a mean of 470 cal (475 and/or 465 cal) for
1 g. We utilized for this approximately 0.25 g. each. Due to
the high density in combination with the high heat of detonation,
cadmium fulminate as explosive shows a particularly high wor-
king density which indicates high shattering power, i.e. high
effective density and/or working density per unit time. Ac-
tually, we found cadmium fulminate to be a substance with ex-
tremely high shattering power. Determination of sensitivity
to temperature increase and impact produced approximately the
same sensitivity as fulminating mercury (ref.5).

2. Thallium Fulminate

100 g amalgam (10-%) obtained from thallium chips and
mercury by direct mixture at room temperature, were shaken in
absolute alcohol -- distilled over barium oxide -- with 1-2
g fulminating mercury in a dark glass under hydrogen for 24
hours. Subsequently, the suspension was elutriated from the
amalgam in a hydrogen stream, repeatedly washed with absolute
alcohol after settling, then liberated from suspended mercury
through elutriation, filtered, covered with absolute ether and
dried in the vacuum dessicator. The white crystalline product
must be protected against moisture because it is easily hydro-
lyzed. It turns superficially yellow under light such as is
the case for some heavy-metal azides (ref.6), a change which

must probably be ascribed as with them to the deposition of finely distributed metal in sunlight but is so minor that composition and specifically explosive properties are changed no more than for the azides. Even small impurities of finely distributed mercury have no influence on the former.

Determination of thallium as oxide after its oxidation produces values which are too low and was therefore made with the iodide (ref. 7). The fulminate is dissolved with diluted sulphuric acid and the accompanying insoluble quicksilver filtered out and weighed; after accurate neutralization of the solution by one-fourth of its volume of 5-% potassium iodide solution, the iodide is precipitated, filtered and air-dried. The principal amount is again dried at 100° in a porcelain crucible and then weighed; the small residue on the filter is dissolved in 2/1-n nitric acid, again precipitared with hydrogen iodide, evaporated and treated exactly as the principal amount. /591

For volumetric determination of fulminate, with silver nitrate, of the thallium fulminate insoluble in alcohol, it was initially converted, by shaking (30 min) with 7-10 ccm of 5-% zinc amalgam (obtained from the metals by heating) per 0.5 g suspended fulminate under 100 cc of absolute methyl alcohol in a small volumetric flask into dissolved zinc fulminate. 25 ccm alcoholic 1/10-silver nitrate solution, completed to 100 ccm and 50 ccm of the filtrate were titered with a 1/10-solution of ammonium thiocyanate and iron solution:

$$Tl \; CNO. \; Ber. \; Tl \; 82.92, \qquad CNO \; 17.08.$$
$$Gef. \quad " \; 82.5, \; 82.7, \qquad " \; 16.90.$$

Heat of explosion is only 223 cal/g but temperature and impact sensitivity is greater than that of fulminating mercury and cadmium and is the largest of all the fulminates with which we are presently familiar. Moreover, nitric acid already initiates explosion. In spite of its particularly high density and sensitivity, thallium fulminate has only minor working density because of the low heat of detonation and relatively low generation of gas and also shows only rather low shattering power (which is measured in practice by the initiating action on explosives) so that we require, under the same conditions, e.g. for detonation of picric acid, 10 times as much as we need of cadmium fulminate or fulminating silver and 20 times as much as lead azide.

3. Cuprofulminate

Cuprofulminate is almost no subject to hydrolytic dissociation because of its insolubility. Its preparation is therefore made by prolonged shaking -- in water and under hydrogen -- of 2 g of suspended silver fulminate with 12-20 ccm of plastic copper amalgam obtained by electrolysis from concentrated sulphate solution on a mercury cathode. Conversion is terminated when the solution of the deposit in sulphuric acid is free of mercury salt after filtration. In order to reduce impurity of the fulminate through finely distributed colloidal mercury which will otherwise color the entire liquid dark brown, we add 2 drops of 2/1-n sulphuric acid before shaking. As protection against oxidation, we wash under hydrogen first with water, then with alcohol and with anhydrous ether and dry under vacuum to constancy.

For determination of copper, we dissolve in cold sulphuric acid and mix with ammonia in order to be able to filter out and weigh admixed metallic mercury which easily amounts to 1% /592 and subsequently boil down with sulphuric acid until the fulminic acid is determined, exactly as for thallium fulminate, after its conversion into soluble zinc fulminate because the cuprous salt reduces directly added silver nitrate to metal.

$$CuCNO.Ber. Cu\ 60.21, \qquad CNO\ 39.79.$$
$$Gef.\ "\ 60.0,\ CO.1,\ 59.8\ "\ 38.9,\ 39.8.$$

Cuprofulminate is very light gray shading slightly into green-- perhaps even white as chloride if it is not influenced by light -- and is stable when kept dry but oxidizes easily in moist air.

Heat of detonation is 508 cal/g. Sensitivity to temperature increase is approximately that of fulminating mercury and cadmium but is less sensitive to impact than the latter. Its density is lower than that of the other heavy-metal fulminates and its working density consequently only slightly higher than that of the thallium salt; its shattering power is appreciably greater. however, and is only slightly below that of cadmium fulminate.

II. Azides

Normal simple and anhydrous azides of the ammonium sulphides have not yet become known. For reasons stated above, however, it is highly desirable to determine their explosive properties and to complete the series of the heavy-metal oxides with them. Only hydrous nickel azide and potassium double

salts of nickel and cobalt are known (ref. 8). The desired salts easily dissociate under hydrolysis due to their solubility and form insoluble salts (ref. 9). The azides of nickel, cobalt, zinc and manganese could be obtained from the carbonates and in ether solution of hydrazoic acid. They are formed without risk if we gradually introduce 5 g of finely divided sodium azide into the mixture of 100 ccm ether and 2 ccm of concentrated sulphuric acid, shake this and filter out the sodium sulphate. If it is inhaled, the solution causes vertigo and headache and must therefore be handled with caution. The action takes place only very slowly and is terminated even with mechanical shaking only after 3 or 4 days; it is more rapid if dry and very finely divided carbonates, i.e. precipitated cold, are utilized. The end of conversion is recognized by the complete solutibility in water of the suspension which is then washed in ether. For zinc azide, an equivalent agent as initial substance is the basic azide made familiar by Curtius and Rissom which must be used for manga- /593 nese because the simple carbonate here reacts too indifferently. Unfortunately, it is impossible to produce anhydrous azides by this method and subsequent drying furnished only the azide of manganese completely and that of zinc almost anhydrous.

Attempts to obtain the normal ferric and chromic azide in similar manner succeeded only imperfectly.

The anhydrous cuprous azide CuN_2 as a further new azide has already been described by us some time ago (ref.10).

The determination of the hydrazoic acid was made according to Curtius and Rissom by distillation with sulphuric acid and titration of a lye of known content; that of the metals in the distillation residue by electrolysis or gravimetry. Calculation covers the anhydrous sum of the two components, that of the water the substance utilized.

1. Nickel Azide

NiN_6. Ber. Ni 41.07,   N 58.98.
     Gef. "   41.3,.41.0 " 57.71, 59.0.

The grainy green powder obtained from ether dissolves easily in water but immediately precipitates in green frakes due to hydrolysis.

It attracts moisture. The bound water -- corresponding to slightly more than 1 mol of reaction water (13%) -- is retained very strongly, partially even after standing for seve-

ral weeks under vacuum alongside phosphorus pentoxide. However, nitrogen is dissociated with measurable speed already at $6C^{\circ}$ so that it cannot be obtained entirely anhydrous without decomposition.

Nickel azide is especially sentisitive to friction. Even slight pressure or rubbing between metal and glass leads to very violent explosion. Preparation and testing therefore require extremely great caution.

2. Cobalt Azide

CoN_6. Ber. Co 41.20, N 58.80
Gef. " 41.36, 41.39, " 58.64, 58.5.

In addition to the reddish brown powder of small rounded crystals of the normal hydrous azide, there originates in ether a red-brown solution (probably an ether - soluble complex cobalt-hydrazoic acid) similar to the cobalt-hydrocyanic acids. Accordingly, not the white azide but a brown-red variant, a complex silver salt, is precipitated with silver solution from this. The water content and its low tension, the tendency to easy decomposition and solubility of the azide in water, as well as its tendency to hydrolysis, are entirely similar to the respective properties of nickel azide. If possible, it is even more sensitive to friction than the nickel salt and detonates easily even between cardboard. Since it has a very high shattering power, the risk in handling it far exceeds that from silver and lead azides.   /594

3. Zinc Azide

ZnN_6. Ber. Zn 43.71, N 56.29, H_2O -
Gef. " 43.68, " 56.34, " 8.25 (after 1-day drying)
" " 43.63, " 56.36, " 0.71 (after 5-day drying).

The hydrous, white, and grainy powder consists of long columnoid crystals, is hygroscopic and can be hydrolyzed like nickel and cobalt azide; in the air, it has a smell of free azoimide and forms a basic salt with water but a clear solution and a complex with hydrogen nitride or sodium azide. Upon ignition, zinc azide smolders only like the alkaline-earth azides and detonates only under strong impact.

Azide is formed also of ethereal azoimide and metallic zinc, but there is simultaneously generated through reduction,
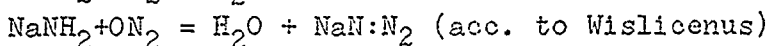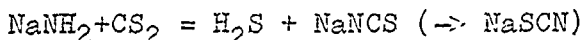
...s in aqueous solution according to Curtius and Darapsky, ammonia, observed earlier (ref. 11) in analogous manner for lead azide, and traces of hydrazine.

4. Manganese Azide

MnN_6. Ber. Mn 39.49, N 60.51, H_2O -.
Gef. " 39.59, " 60.42, " 3.07 (after 2-day drying)
" " 39.39, " 60.61, " - (after 5-day drying)

The grainy crystalline white and normal azide produced from the amorphous basic azide, after brief shaking with the ethereal acid, is hygroscopic and oxidates to black-brown dihydroxide, through hydrolysis which takes place very rapidly under dry heating to 100°. The azide is more sensitive and has a greater shattering power than the zinc salt, without attaining the high sensitivity of the cobalt and nickel azides.
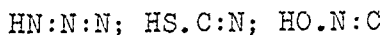
5. Ferric Azide

If dry ferric sulphate is shaken in absolute methyl alcohol with sodium azide and the deep dark-red solution evaporated under vacuum alongside of potash and phosphorus pentoxide, we then obtain hygroscopic black-brown flakes, as residue, which hydrolyze under dissolution in water by dissociation of azoimide and therefore produce also a somewhat too low /595 nitrogen content in the analysis.

FeN_9. Ber. Fe 30.66, N 69.34.
Gef. " 32.18, 33.17," 67 83,66.84.

The characteristic intensive red coloration of the solution so much recalls that of the ferric-thiocyanate complex that it suggests, together with a comparison of the analogous formation of both sodium salts:

$NaNH_2+CS_2$ = H_2S + NaNCS (→ NaSCN)

$NaNH_2+ON_2$ = H_2O + NaN:N_2 (acc. to Wislicenus)

the analogy with the 4-member thiocyanic acid or, more correctly, of the isothiocyanic acid. It thus constitutes new support for the Agenli-Thiele assumption of the open constitution of the hydrazoic acid and at the same time thus established a bridge to the similarly constituted fulminic acid with analogous explosive properties:

HN:N:N; HS.C:N; HO.N:C

6. Chromic Azide

From chromic hydroxide precipitated cold, we obtain, by shaking with an alcoholic hydrazoic acid, a dark-green solution and, after evaporation of the latter under vacuum, a black-green hygroscopic mass. Its clear solution becomes turbid only after boiling and, with silver solution, does not produce a white but a green azide so that a complex oxide exists whose content of chromium and nitrogen lies between that of an azido-acid $(Cr(N_3)4)$ and a "basic" hydrazoic acid $(Cr(N_3)3Oh)H$. The substance was not further investigated since it explodes only moderately like ferric azide and thus has no significance for our purposes at the moment.

$$[Cr(N_3)_3OH.] \text{ H.} \quad \text{Ber. Cr 29 20,} \quad \text{N 70.80.}$$
$$[Cr(N_3)_4] \text{ H.} \quad \text{Ber. Cr.27.08,} \quad \text{" 72.92.}$$
$$\text{Gef. " } 27.86, 27.81, \text{ N } 72.13, 72.19.$$

For comparison, we list in conclusion the specific detonation heat of the new azides together with those of some known azides as well as those of the known and of the new heavy-metal fulminates which we determined as described.

	cal/g		cal/g
Silver Azide	452	Manganese Azide	676
Lead Azide	364	Calcium Azide	625
Cuprous Azide	582	Strontium Azide	295
Mercurous Azide	266	Silver Fulminate	470
Cadmium Azide	558	Cupro-Fulminate	508
Thallous Azide	232	Thallous Fulminate	223
Nickel Azide	656	Cadmium Fulminate	470
Zinc Azide	360	Mercury Fulminate	397

Summary

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1. The previously unknown simple fulminates of cadmium, thallous oxide and cuprous oxide were prepared with the aid of amalgams from silver and mercury fulminate and characterized.

2. From carbonates or basic azides, we newly obtained with ethereal azoimide solution, in addition to the already known hydrous nickel azide, cobalt, zinc and manganese azide whereas ferric and chromic azide were produced as non-uniform complexes.

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